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Doping kinetics of organic semiconductors investigated by field-effect transistors

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The kinetics of acid doping of the semiconductor regioregular poly-3-hexylthiophene with vaporized chlorosilane have been investigated using field-effect transistors. The dopant density has been derived as a function of temperature and exposure time from the shift in the pinch-off voltage, being the gate bias where current starts to flow. The doping kinetics are perfectly described by empirical stretched exponential time dependence with a saturation dopant density of $1 \pm 0.5 \times 10^{26} \text{ m}^{-3}$ and a thermally activated relaxation time. We show that a similar relationship holds for previously reported kinetics of poly-thienylene-vinylene doped with molecular oxygen. © 2010 American Institute of Physics. [doi:10.1063/1.3466903]

Upon exposure of organic field-effect transistors to gases, changes have been observed in key transistor parameters such as threshold voltage and field-effect mobility.^{1,2} The most dominant change, however, is a change in the conductance due to chemical doping of the semiconductor. A gas sensor could be envisaged by monitoring the increase in conductance upon exposure to the target analyte.³

To fabricate a reliable gas sensor it is important to understand the *kinetics* of the doping process. However, the number of studies on the doping kinetics is limited. Most studies focus on the conductivity of organic semiconductors as a function of dopant density.^{4,5} The increase in the conductivity with time has only been investigated for regioregular poly-3-hexylthiophene (rr-P3HT) and poly-thienylenevinylene (PTV) exposed to molecular oxygen.⁶ From analysis of the transfer curves the dopant density and bulk mobility could be derived as a function of exposure time. The study was performed to analyze the shelf-life of organic transistors.

In order to understand the kinetics of the doping of organic semiconductors, we initially doped rr-P3HT in field-effect transistors with gaseous HCl. At the partial vapor pressures used however, the doping process was much too fast to reliably determine the kinetics; the polymer was fully doped and highly conductive in a matter of minutes. To expand the time scale and have a better control over the doping process of the semiconductor, we used vaporized trichloro-(1*H*, 1*H*, 2*H*, 2*H*)-perfluorooctylsilane (TCFOS). This molecule is reported to yield acid doping of conjugated molecules.³ We found that the doping process of rr-P3HT with TCFOS is sufficiently slow to measure the doping kinetics. The dopant density is derived from the transfer curves as a function of temperature and exposure time. We show that the kinetics can phenomenologically be described with stretched exponential time dependence and that the same relationship holds for previously reported doping studies.⁶

Field-effect transistors were made on n^{++} -Si substrates acting as a common gate. A 200 nm oxide layer passivated

with hexamethyldisilazane was used as gate dielectric. Gold source and drain electrodes with a thickness of 100 nm on a 5 nm Ti adhesion layer were defined by photolithography. rr-P3HT (Rieke Chemicals, purified by Soxhlet extraction) was dissolved in chloroform (2% w/v) and spincoated on top of the prefabricated substrates. The rr-P3HT films were annealed at 150 °C in vacuum for 2 h. Transfer and output characteristics of the transistors were recorded in the dark using a Keithley 4200 semiconductor parameter analyzer. The measurement chamber was evacuated to less than 10^{-4} mbar. Then 20 μL TCFOS (Sigma Aldrich) was injected into an antechamber. The valve to the measurement chamber was opened yielding a TCFOS partial pressure of $\sim 2.5 \times 10^{-2}$ mbar and the transistors were measured as a function of temperature and exposure time. Without TCFOS the transfer curve does not change with time; stress can be disregarded on the timescale of the experiment.

The transfer curves at different times of exposure to TCFOS at room temperature are presented in Fig. 1(a). The curves shift toward positive gate bias with exposure time. Furthermore a shoulder appears and the on-current in accumulation slightly increases. We note that the off-current in depletion increases as well, which is due to increased parasitic leakage currents outside of the defined transistor area caused by the use of unshielded drain electrodes.⁶ The analy-

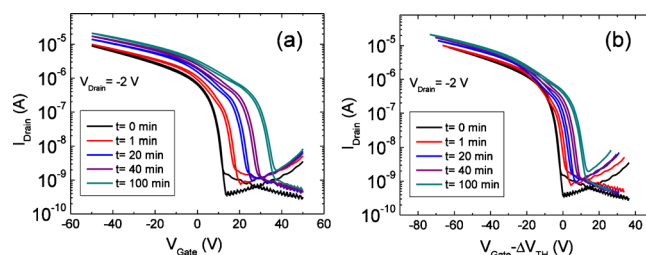


FIG. 1. (Color online) (a) Transfer curves in the linear regime of a rr-P3HT organic field-effect transistor in vacuum and after exposure to TCFOS vapor at room temperature for different exposure times. The channel length and width are 10 μm and 10 000 μm , respectively. (b) The transfer curves corrected for the threshold voltage shift with respect to the pristine undoped transistor at $t = 0$ s.

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sis of the shift in the transfer curves toward positive gate bias with exposure time is complicated by the fact that two effects have to be disentangled. Initially, the doping process can lead to the formation of charged states at the interface between the insulator and the semiconductor. This will lead to a shift in the threshold voltage. Furthermore, upon exposure to TCFOS the rr-P3HT gets chemically doped and a higher positive bias is needed to deplete the bulk semiconductor. To get a quantitative result for the threshold voltage shift between the measurements we linearly extrapolated the current as a function of the gate bias for each measurement on a linear scale and determined from the intercept the threshold voltage. The transfer curves corrected for the threshold voltage shift are presented in Fig. 1(b) and show a cross-over from an accumulation mode into a bulk depletion mode transistor. The current in accumulation, at negative bias, is dominated by the channel current while in depletion, at positive bias, the current is mainly flowing through the bulk semiconductor. The remaining shift in the transfer curves now arises from the doping and is characterized by a shift in the pinch-off voltage. At the pinch-off voltage, defined as the gate bias where current starts to flow, the bulk semiconductor is fully depleted. When the gate bias is sufficient to enable charge accumulation in the channel the current increases superlinearly with gate bias, which is manifested by the shoulder in the transfer curve. This superlinear increase is due to the fact that the charge carrier mobility in the channel is much larger than in the bulk. This difference in charge carrier mobility originates from the fact that the mobility is charge density dependent⁷ and the charge density in the channel is much larger than in the bulk of the semiconductor.

The dopant density, N_A , can be determined from the following pinch-off voltage (V_{PO}) as described previously by the following:⁶

$$N_A = \frac{2V_{PO}\epsilon_0}{q\left(\frac{d_S^2}{\epsilon_S} + \frac{2d_S d_I}{\epsilon_I}\right)}, \quad (1)$$

where ϵ_I and ϵ_S are the relative dielectric constants for the insulator and semiconductor, respectively, d_I and d_S are the layer thickness for the insulator and semiconductor, respectively, and q is the elementary charge. The dopant densities calculated with Eq. (1) using the pinch-off voltages extracted from Fig. 1 are presented in Fig. 2 on a double logarithmic scale as a function of time. Values for the dopant densities derived at other temperatures are included as well.

Figure 2 shows that the dopant density increases with time as a power law. The exponent however, increases with temperature. This dependence suggests that the time and temperature dependence can phenomenologically be described by a single stretched exponential:

$$N_A(t) = N_A(t \rightarrow \infty) \left(1 - \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \right), \quad (2)$$

where $N_A(t \rightarrow \infty)$ is the saturation dopant density, β is a dispersion parameter typically equal to T/T_0 , with T being the absolute temperature and T_0 a characteristic temperature, and τ being the average relaxation time constant. The solid lines in Fig. 2 represent a simultaneous fit to all the data points. A good agreement is obtained with $N_A(t \rightarrow \infty) = 1 \pm 0.5 \times 10^{26} \text{ m}^{-3}$ and $T_0 = 690 \pm 40 \text{ K}$. The value for the satura-

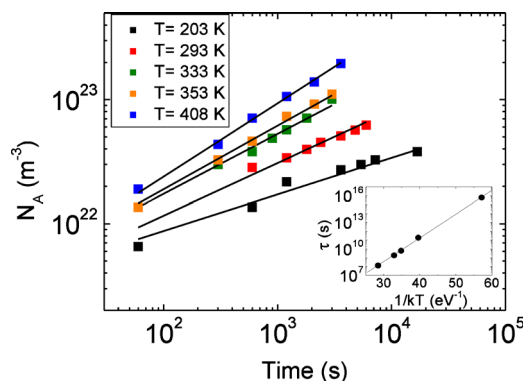


FIG. 2. (Color online) Dopant density vs exposure time at different temperatures for rr-P3HT doped with silane (TCFOS) vapor. The solid lines are a simultaneous fit to the data with a stretched exponential time and temperature dependence. The inset shows the relaxation τ as a function of reciprocal temperature.

tion dopant density derived indicates that about 10% of the thiophene units can be chemically oxidized. This number is in good agreement with the maximum doping level derived from electrochemical studies; in polythiophene about one out of every four monomeric units can be oxidized.⁸ The inset of Fig. 2 shows that the relaxation time, τ , is thermally activated. The activation energy of 0.6 eV, or about 58 kJ mol⁻¹, agrees with reported values for protonation reactions of organic molecules,^{9–12} suggesting acid doping of rr-P3HT by TCFOS.

The doping of rr-P3HT was investigated at different partial pressures of TCOFS, viz., 2.5×10^{-2} and 2.5×10^{-1} mbar. The main effect is a decrease in the relaxation time with increase in TCOFS partial vapor pressure, indicating that increasing the pressure of the dopant increases the speed of the doping of the semiconductor.

Doping of PTV exposed to molecular oxygen in field-effect transistors has previously been reported.⁶ Similar to this study the dopant density has been derived as a function of partial oxygen pressure and exposure time but the doping kinetics were not further analyzed. Here, we replot the reported values in Fig. 3; the fully drawn curves are a stretched exponential fit to the data using Eq. (2). Also for the oxygen doping of PTV a good agreement is obtained. For the fit we used the same maximum dopant density, $N_A(t \rightarrow \infty)$, as derived above for rr-P3HT. The characteristic temperature T_0 follows directly from the slope of dopant density versus time

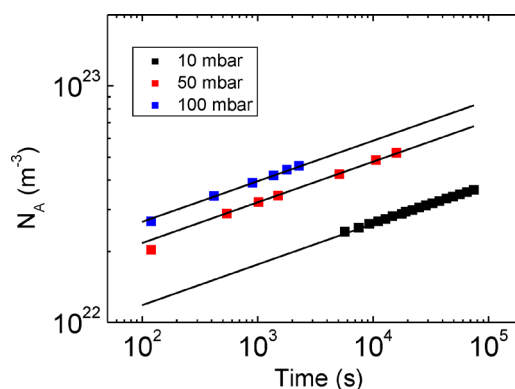


FIG. 3. (Color online) Dopant density vs time at different temperatures for PTV doped with molecular oxygen at different pressures. The solid lines are the fit with a stretched exponential relationship.

and amounts to $T_0 = 1700 \pm 30$ K. The dopant density has not been reported as a function of temperature in the PTV study. Hence we can determine the average relaxation time τ but not the activation energy. We find that τ is inversely proportional to the oxygen pressure, $\tau \sim p_{\text{O}_2}^{-1.4}$. When we assume that the activation energy does not depend on oxygen pressure, the relation between τ and pressure can then be rationalized by a prefactor that increases with oxygen pressure.

The electrical transport in organic semiconductors is dominated by thermally activated hopping between localized states at the Fermi level.^{7,13,14} When the effect of doping on the charge transport is only governed by filling up of transport states with the charge carriers that are released from the dopants, it can be expected that the characteristic temperature derived from the doping study would be similar to the isokinetic temperature characterizing the electrical transport states. However, the differences obtained, viz., 690 and 425 K for rr-P3HT and 1700 and 380 K (Ref. 15) for PTV, indicates that chemical doping creates additional states in the band gap, as confirmed by numerous optical absorption investigations.

In summary, we have investigated acid doping of rr-P3HT with silane TCFOS vapor in field-effect transistors. The transfer curves shift toward positive gate bias, into depletion, upon exposure time. The dopant density has been derived from the shift in pinch-off voltage as a function of temperature and exposure time. The dopant density kinetics can phenomenologically be described by stretched exponential time dependence. The doping is thermally activated with activation energy of about 0.6 eV, which agrees with reported values for protonation reactions of organic molecules. Rein-

terpretation of reported doping densities as a function of time for PTV doped with molecular oxygen showed the same relationship. The good agreements obtained indicate that the doping kinetics of organic semiconductors follows stretched exponential time dependence.

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